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Alkyd resin emulsions and uses thereof

The present invention relates to a two-component water paint system and a process for its production.

In conventional aqueous two-component polyurethane paints, CO_2 is formed in the side reaction of the isocyanate with water which leads to the undesired formation of bubbles in the paint film. According to the presently known prior art, such systems allow the reliable production of layer thicknesses of at most 60 – 80 μm , depending on the degree of pigmentation and the drying conditions. The two-component water paint system of the present invention on the other hand is especially characterized by low degree of bubble formation. This allows the production of layers having a thickness of at least 120 μm , often at least 150 μm without any undesired bubble formation.

Due to ecological problems and the resulting necessity of reducing solvent emissions, water-dilutable paints have been widely used and in many fields of application replaced solvent-containing paints and coatings.

For years, aqueous two-component polyurethane systems have proved to be worthwhile in those fields of application which require a high degree to weathering resistance, corrosion control and chemical resistance. These two-component systems comprise a polyol component and an isocyanate component which are mixed shortly before processing. Usually, oligomeric polyisocyanates, e.g. on the basis of hexamethylene diisocyanate and isophorone diisocyanate, are used as isocyanate components. Hydroxy-functional polyacrylate primary and secondary dispersions, water-soluble or water-emulsible polyester and hydroxy-functional polyurethane dispersions are primarily used as polyol component.

These paint systems are increasingly used e.g. as automotive paints and as lacquers for plastics and furniture. In many cases, the problem of unreliability of the process prevented a more widespread application. In particular in the case of high layer thicknesses and unfavorable climatic conditions such as e.g. high humidity, a strong formation of bubbles takes place due to the CO_2 formed in the side reaction of the isocyanate with water during drying.

The object underlying the present invention is to provide a two-components water paint system showing only a low tendency to form bubbles and suitable for producing bubble-free paint layers having a thickness of at least 120 μm , preferably at least 150 μm .

This object is achieved by a two-component water paint system comprising an isocyanate components and an aqueous emulsion of a hydroxy-functional alkyd resin. The hydroxy-functional alkyd resin can be obtained from an oleic or fatty acid components, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof.

The water paints of the present invention are suitable to be applied to different substrates such as e.g. plastic materials, metal and wood.

Furthermore, the invention provides a process for the production of the inventive two-component water paint system comprising

- 1) providing an isocyanate component,
- 2) preparing an aqueous emulsion of a hydroxy-functional alkyd resin comprising:
 - a) reacting an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof to obtain a hydroxy-functional alkyd resin,
 - b) neutralizing the alkyd resin with ammonia or amine,
 - c) emulsifying the alkyd resin in water.

Similar alkyd resin emulsions are in principle already described, e.g. in US-A-3,442,835, however, they have been exclusively employed as binding agents in air-drying or baking single-component paints. Single-component paints essentially differ from two-component paints in their level of quality. Two-component polyurethane paints are clearly superior to alkyd-based air-drying single-component paints in terms of mechanical properties such as flexibility and hardness but also with respect to weathering resistance, and resistance to solvents and environmental exposure (cf. *Farbe & Lack*, 2/98, page 85).

The alkyd resin of the present invention is prepared from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof.

Preferably, the alkyd resin comprises 10 to 70 wt.-%, particularly preferred 15 to 40 wt.-%, of an oleic or fatty acid component, 10 to 35 wt.-%, particularly preferred 10 to 30 wt.-%, of a polyvalent alcohol having 2 to 6 hydroxyl groups, 3 to 15 wt.-%, particularly preferred 3 to 8 wt.-%, of a polyether polyol having a molecular weight of 400 to 8,000, in particular 1,000 to 6,000, 0 to 25 wt.-%, particularly preferred 10 to 20 wt.-%, of a monobasic carboxylic acid having 6 to 18 carbon atoms, and 10 to 35 wt.-%, particularly preferred 15 to 30 wt.-%, of a dicarboxylic acid having 4 to 10 carbon atoms or the anhydride thereof. Optionally, up to 10 wt.-% of a polybasic

carboxylic acid such as e.g. trimellitic acid or the anhydride thereof can be present in the production of the hydroxy-functional alkyd resin.

Preferably, natural oils or their fatty acids, in particular non-drying oils or their fatty acids, which are characterized by good weathering resistance and a low tendency to yellowing, are used as oleic or fatty acid components. The non-drying oils used in the present invention include all natural oils which are usually employed in the production of alkyd resins. The term "non-drying oil" in this connection refers to a triglyceride of fatty acids which usually have 10 to 24 carbon atoms per molecule and an iodine number of <110. Mixtures are also encompassed by the present invention.

Suitable oils include vegetable oils such as apricot kernel oil, peanut oil, kapok oil, coconut oil, almond oil, olive oil, palm oil and castor oil. Peanut oil, coconut oil and castor oil are preferred.

The amount of oil used in the present invention can vary from 10 to 70 wt.-%, preferably 15 to 40 wt.-%, of the final product.

The term oils also includes esters of fatty acids with 10 to 24 carbon atoms with triols, such as trimethylolethane and trimethylolpropane, wherein the molar ratio of fatty acid to triol is 3:1. According to the present invention, the oils can be employed as such or as ester-forming precursors such as fatty acids and triols, wherein the ester is formed in situ. Furthermore, mixtures of different oils can be used as oleic or fatty acid components.

The monobasic carboxylic acid used in the present invention has 6 to 18 carbon atoms per molecule and includes saturated aliphatic acids, saturated cycloaliphatic acids and aromatic acids. Typical examples include isodecanoic acid, isoctanoic acid, cyclohexanoic acid, cyclopentanoic acid, benzoic acid, p-tert.-butylbenzoic acid and long-chain fatty acids derived from substances like coconut oil, palm kernel oil, babassu oil and other fats and oils known in the technical field. Mixtures of these acids can be used as well. Preferably, benzoic acid and p-tert.-butylbenzoic acid are used. The amount of the acids used in the present invention is about 0 to about 25

wt.-%; preferably about 10 to about 20 wt.-%, of the alkyd resin. Mixtures of the monobasic carboxylic acids are also encompassed by the present invention.

The dicarboxylic acids used in the present invention and their anhydrides have 4 to 10 carbon atoms per molecule and include aliphatic, cycloaliphatic and aromatic dicarboxylic acids and their anhydrides. Examples of these acids or anhydrides include maleic acid, fumaric acid, terephthalic acid, isophthalic acid, adipinic acid, glutaric acid, azelaic acid and phthalic acid or the anhydrides of these compounds. The amounts thereof used in the present invention are about 10 to about 35 wt.-%, preferably about 15 to about 30 wt.-%, of the alkyd resin. Especially preferred are phthalic acid, isophthalic acid and adipinic acid as dicarboxylic acid or anhydride. Mixtures of the dicarboxylic acids are also encompassed by the present invention.

The polyvalent alcohols used in the present invention have at least 2, however, not more than 6, hydroxy groups per molecule and 2 to 8 carbon atoms. Examples of these polyvalent alcohols include ethylene glycol, diethylene glycol, glycerine, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol, sorbitol, mannitol and similar polyvalent alcohols which can be used for the preparation of alkyd resins. Mixtures of these polyvalent alcohols can also be used. Particularly preferred polyvalent alcohols are glycerine, pentaerythritol and trimethylolpropane. Mixtures of polyvalent alcohols are encompassed by the present invention.

In order to increase emulsibility, about 3 to about 15 wt.-%, preferably about 3 to about 8 wt.-%, of polyether polyols such as polyethylene glycol, polypropylene glycol or polytetrahydrofuran are incorporated in the alkyd resin. Preferably, the polyoxyethylene glycols of the present invention comprise a long chain of repeating oxyethylene units with a hydroxy group at each end of the chain. The preferred average molecular weight of the used polyglycols is about 400 to about 8,000, preferably about 1,000 to about 6,000. Mixtures of polyether polyols are also encompassed by the present invention.

As is common in alkyd resin chemistry, the alkyd resin can be prepared in a one-step or two-step process.

In the one-step process, the oleic or fatty acid component, the monocarboxylic acid, the polyvalent carboxylic acid or the anhydride are esterified with the polyalcohols and the polyether alcohol at temperatures from 180 to 260°C until an acid number of 3 to 80 KOH/g, preferably 8 to 20 KOH/g, is reached.

The two-step process usually starts from the natural oil which is reacted with polyalcohols at temperatures from 180 to 260°C until the desired degree of transesterification is reached. In the second step, this reaction product is esterified with the mono and polycarboxylic acids and the polyether alcohol at 200°C to 260°C, while water is eliminated, until an acid number of 3 to 80 mg KOH/g, preferably 8 to 20 KOH/g, is reached. The acid number can be determined by means of a method according to DIN 53402.

In the case that the oleic or fatty acid component is formed in situ from precursors, e.g. fatty acid and triol, a one-step process is preferred.

Preferably, the hydroxyl content of the inventive alkyd resin is 1 to 8 wt.-% based on the alkyd resin. Resins with a low hydroxyl content require smaller amounts of the expensive isocyanate for curing while resins with a high hydroxyl content require higher amounts of isocyanate, however, the latter exhibit a superior chemical resistance. As is common in the technical field, the hydroxyl content can be determined by reaction with acetic acid anhydride.

For increasing the initial molecular weight and for improving physical drying or accelerating initial drying the alkyd resin can be pre-cured with isocyanates. However, during the modification of the hydroxy-functional alkyd resin with isocyanate no more than 30% of the available hydroxyl groups should be reacted.

Mono-, di- or triisocyanates alone or in admixture can be used for modifying the hydroxy-functional alkyd resin by means of pre-curing with isocyanate. Examples of the isocyanates used in the present invention include toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, 3-phenyl-2-ethylene diisocyanate, 1,5-naphthalene diisocyanate, cumene-2,4-diisocyanate, 4-methoxy-1,3-diphenyl diisocyanate, 4-chloro-1,3-phenyldiisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-

2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate, 4-bromo-1,3-phenyl-diisocyanate, 4-ethoxy-1,3-phenyl diisocyanate, 2,4'-diisocyanatodiphenylether, 5,6-diisocyanate, 2,4-dimethyl-1,3-phenyldiisocyanate, 4,4'-diisocyanatodiphenylether, 4,6-dimethyl-1,3-phenyldiisocyanate, 9,10-anthracene diisocyanate, 2,4,6-toluene triisocyanate, 2,4,4'-triisocyanatodiphenylether, 1,4-diisocyanate, 1,6-hexamethylene diisocyanate, 1,10-decamethylene tetramethylene diisocyanate, 1,3-cyclohexylene diisocyanate, 4,4'-methylene-bis(cyclohexylisocyanate), xylenediisocyanate, 1-isocyanato-3-methylisocyanato-3,5,5-trimethylcyclohexane (isophoronediisocyanate), 1,3-bis(isocyanato-1-methylethyl)-benzene (m-TMXDI) and 1,4-bis(isocyanato-1-methylethyl)benzene (p-TMXDI). Preferably, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate, 1,6-hexamethylene diisocyanate and isophorone diisocyanate are used in the present invention. The reaction with isocyanate usually takes place in the temperature range from 10 to 70°C, preferably 20 to 50°C.

After neutralization with ammonia or amines, the alkyd resins according to the present invention can be emulsified in water without the addition of solvents. The resulting emulsions usually have a solids content of 20 to 70%, preferably 30 to 55%, and a pH value of 6 to 9.

Neutralization can be achieved by adding a small amount of a neutralizing agent which neutralizes a part or all of the acid groups in the resin.

Suitable neutralizing agents which can be used in the present invention include ammonia, ammonium hydroxide and primary, secondary and tertiary mono- or polyamines, including hydroxyamines and in particular low alkylamines, such as ethylamine, butylamine, dimethylamine, diethylamine, dimethylethylamine, dimethyl-ethylamine, diethanolamine, triethanolamine, aminopropanol, dimethylamino-isopropylamine, diethanolamine, triethanolamine, triisopropanolamine, ethanolamine, dimethyl-propanol, tributylamine, triethylamine, triisopropanolamine, ethanolamine, dimethyl-ethanolamine or butanolamine. Amines which are volatile at temperatures below 180°C, preferably 120°C, are preferred. Especially preferred amines include ammonia, triethylamine, dimethylethylamine, dimethylisopropylamine, dimethyl-ammonia, triethylamine, diethanolamine, triethanolamine, aminopropanol and ethanolamine, ethanolamine, diethanolamine, triethanolamine, aminopropanol and ethanolamine.

dimethylaminopropanol. The amines can be added in undiluted form wherein essentially anhydrous neutralized resin products are obtained which can be diluted with water or dispersed in water basically without restrictions. Alternatively, the resins can be neutralized by the addition of an aqueous solution or dispersion of amines. Inorganic neutralizing agents such as potassium or sodium hydroxide or carbonates can be used as well. Mixtures of neutralizing agents can also be used.

The resin is then adjusted to a certain viscosity in water and an aqueous dispersion with 5 to 55 wt.-%, preferably 25 to 55 wt.-%, resin solids (non-volatile) is obtained.

Subsequently, the described alkyd resin emulsions can then be formulated to give pigmented or unpigmented parent paints by means of additives commonly used in the paint industry, such as pigments, filler materials and auxiliary agents.

These alkyd emulsions are characterized by excellent stability in the pH range from 6 to 9 and are very suitable for formulating aqueous two-component paints.

Shortly before processing the curing agent, i.e. the isocyanate, is added to the parent paint and mixed in either manually or mechanically to give a homogeneous mixture. The compounds listed as pre-curing agents are suitable as isocyanate. However, especially suitable are oligomeric polyisocyanates as used in conventional solvent-containing two-component polyurethane paints. They include for example pre-adducts, isocyanurates, uretdiones, allophanes and the like on the basis of hexamethylene diisocyanate, isophorone diisocyanate and toluylene diisocyanate. Oligomeric polyisocyanates comprising hydrophilic components which were formulated specifically for the use in water paint systems are also suitable. Such isocyanate components are for example described in the patents EP-B1-0 540 958, EP-B1-0 645 410, EP-A2-0 754 713 and EP-A1-0 697 424.

An organic solvent such as e.g. an ester, a ketone or an alkylated ester of polyvalent alcohols or oligomeric polyglycols, such as methoxypropyl acetate, methoxydiglycol acetate or the like can be added to the isocyanate component in order to improve its incorporation or to decrease the viscosity. The amount of solvent is usually in the range of 10 to 40 wt.-%, based on the used isocyanate.

The mixing ratio of parent paint and isocyanate curing agent depends on the number of hydroxyl groups in the polyol component and the NCO content in the isocyanate component. The stoichiometric ratio is calculated based on the basic isocyanate value, which defines the amount of polyisocyanate which is equivalent to 100 parts by weight of the hydroxy group containing components.

$$\text{basic isocyanate value} = \frac{42 \times 100 \times \text{OH \% in the polyol component}}{17 \times \text{NCO \% in the isocyanate component}}$$

In practice, this basic isocyanate value works as a guide value. Depending on the desired properties of the paint system, the amount of curing agent can be varied considerably. Usually, markedly higher isocyanate amounts are used in water paints since for example part of the isocyanate reacts with water to form polyureas and is then no longer available for cross-linking with the polyol component.

Depending on its composition, this mixture has a processing time from 10 minutes to 6 hours at room temperature. The paint is either cured at room temperature or under forced drying conditions like heating. The reaction can be accelerated by means of catalysts common in polyurethane chemistry, e.g. metal salts, amines and the like.

Surprisingly, the two-component water paint systems of the present invention allows the production of paint layers with a thickness of more than 120 μm and even more than 150 μm without the formation of bubbles, even under unfavorable climatic conditions such as increased humidity. Thus, high quality coatings can be produced with the systems of the present invention which match those produced with conventional solvent-containing two-component polyurethane paint, particularly as far as resistance and mechanical properties such as for example hardness, flexibility, adhesion and the like are concerned.

The following examples illustrate the invention.

Example 1

100 g peanut oil, 38 g polyethylene glycol, 78 g para-tert-butylbenzoic acid and 75 g pentaerythritol are heated at 230°C for 3 hours. Then, 126 g phthalic acid anhydride and 38 g pentaerythritol are added and the reaction mixture is esterified at temperatures of 180 to 250°C, while water is eliminated, until an acid number of 10 to 20 mg KOH/g is reached.

The reaction mixture is neutralized with triethylamine and emulsified in 550 g water. A finely divided emulsion with a solids content of about 45 wt.-% and a pH value of about 7 is obtained.

Example 2

The alkyd resin emulsion obtained in Example 1 is used to prepare a white finish according to the following formulation.

- A 33.3 parts by weight alkyd emulsion from Example 1
- B 27.8 parts by weight titanium dioxide
- C 0.7 parts by weight dispersion additive
- E 26.7 parts by weight alkyd emulsion from Example 1
- F 8.5 parts by weight water

The mixture of A, B and C is dispersed by means of a stirred ball mill. Then components E and F are added.

Example 3

The parent paint prepared in Example 2 is mixed in a weight ratio of 4:1 with an isocyanate curing agent of the following composition

- 70 parts by weight polyisocyanate based on hexamethylene diisocyanate and
- 30 parts by weight methoxypropyl acetate

The paint/curing agent mixture has a processing time of about 4 hours and can be processed to give a dry layer thickness of up to 180 μm without any undesired formation of bubbles due to the release of CO_2 . Drying takes place overnight or in a forced manner for about 30 minutes at 80 to 100°C. Suitable substrates include e.g. plastic materials, metal and wood.

Example 4

Clear lacquer alkyd emulsion basis as furniture or parquetry sealing

87 g alkyd emulsion from Example 1
2 g flow-control additives
2 g butyldiglycol acetate and
9 g water

are mixed homogeneously.

Prior to processing, the isocyanate component of Example 2 is added in a ratio of 3:1.

The paint can be processed up to a dry layer thickness of 150 μm without the formation of bubbles. The processing time is about 4 hours. Curing time at room temperature is about 15 hours. Forced drying at about 80°C is possible.